Supporting Information for "Reversible H_2 Addition Across a Nickel–Borane Unit as a Promising Strategy for Catalysis"

*W. Hill Harman and Jonas C. Peters**

Contents

Experimental Part

General considerations. Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Solvents were dried and deoxygenated by sparging with dinitrogen and passage through activated alumina in a solvent purification system from SG Waters USA, LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. $^{Ph}DPB^{Ph}$ (**1**), [1] (2-diphenylphosphino)bromobenzene, [2] and mesityldichloroborane[3] were synthesized by previously reported procedures. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3Å molecular sieves prior to use. ^1H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane using residual solvent ^1H and ^{13}C resonances as internal standards. ^{31}P and ^{11}B chemical shifts are reported in ppm relative to 85% aqueous H_3PO_4 and $BF_3{\cdot}Et_2O$, respectively. Solution effective magnetic moments (μ_{eff}) were determined by Evans' method.[4] Optical spectroscopy measurements were taken on a Cary 50 UV-vis spectrophotometer using a 1 cm two-window quartz cell.

X-ray crystallography. Single crystal X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility on a Bruker Kappa Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å). Crystals were mounted on glass fibers. Structures were solved using SHELXS and refined against F^2 on all data by full-matrix

[1] Sircoglou, M.; Bontemps, S.; Mercy, M.; Saffon, N.; Takahashi, M.; Bouhadir, G.; Maron, L.; Bourissou, D. *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 8583.
[2] Whited, M. T.; Rivard, E.; Peters, J. C. *Chem. Commun.* **2006**, 1613.
[3] Sundararaman, A.; Jäkle, F. *J. Organomet. Chem.* **2003**, *681*, 134.
[4] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

least squares with SHELXL. Relevant details for individual data collections are reported in Tables S3–6.

Computational methods. Geometry optimizations were performed using the Gaussian03 package.[5] The relative energies of reasonable isomers of the postulated structure were first compared using the BP86 functional with a 6-31G(d) basis set. After locating an unambiguous global minimum, the resulting structure was further optimized with the B3LYP exchange-correlation functional with a 6-31G(d) basis set. The GDIIS algorithm was used. A full frequency calculation was performed on each structure to insure convergence to a true minimum. Geometry optimizations were begun at pseudo-tetrahedral starting points.

[^{Ph}DPB^{Ph}]NiBr (2). $Ni(cod)_2$ (46 mg, 170 μmol) and $NiBr_2$ (37 mg, 170 μmol) were added consecutively as solids to a stirring solution of **1** (206.0 mg, 337 μmol) in THF (12 mL) resulting in the formation of a dark mixture which became dark orange-red over the course of an hour. After stirring for six hours at room temperature, the volatiles were removed from the reaction *in vacuo* and the residue dissolved in CH_2Cl_2 (2 mL). After filtration to remove a small amount of insoluble material, pentane was layered over the filtrate to give deep orange-red crystals of the title compound that were separated from the mother liquor and dried *in vacuo* (180 mg, 71%). Crystals grown in this manner were suitable for X-ray diffraction. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 17.6, 17.0, 9.4, 4.7, 3.2, 0.1, –2.4. Anal. Calcd for $C_{42}H_{33}BBrNiP_2$: C, 67.34 H, 4.44. Found: 67.43, 4.64. μ_{eff} = 1.6 B.M.

[^{Ph}DPB^{Ph}]Ni(THF) (3). Sodium (15 mg, 650 μmol) and mercury (1.5 g) were added to a scintillation vial, covered with THF (1 mL) and stirred vigorously. A solution of **2** (179 mg, 239 μmol) in THF (10 mL) was added. After 2 hours, the dark green mixture was decanted from the mercury, filtered and concentrated to ~2 mL *in vacuo*. Pentane was diffused into this solution to afford dark green crystals of the title compound that were separated from the mother liquor and dried *in vacuo* (147 mg, 83%). Crystals grown in

[5] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

this manner were suitable for X-ray diffraction. ^{1}H NMR (300 MHz, THF-d_8) δ 8.04 (d, J = 7.7 Hz, 2H), 7.58 (m, 4H), 7.32 (s, 6H), 7.23 (m, 4H), 7.11 (m, 4H), 7.04 (m, 4H), 6.91 (m, 4H), 6.83 (m, 5H), 3.54 (s), 1.68 (s). ^{13}C{^{1}H} (75 MHz, $CDCl_3$) δ 139.4, 139.2, 134.5, 133.8, 132.8, 131.7, 131.1, 129.5, 129.0, 128.6, 127.9, 125.9, 125.0, 68.3, 26.4. ^{31}P{^{1}H} NMR (121 MHz, THF-d_8) δ 27.4 (s). Anal. Calcd for $C_{46}H_{41}BNiOP_2$: C, 74.53 H, 5.57. Found: 73.94, 5.69.

MesB(*o*-PPh$_2$C$_6$H$_4$)$_2$ ([^{Mes}DPB^{Ph}], 4). A stirring suspension of 2-diphenylphosphinobromobenzene (6.11 g, 17.9 mmol) in Et_2O (50 mL) was cooled to –78 ºC and *n*-BuLi (11.2 mL, 1.6 M in hexanes, 18 mmol) added dropwise. The resulting mixture was stirred for 30 minutes at –78 ºC and allowed to warm to room temperature. The solvent was removed *in vacuo* and the residue was dissolved in toluene (50 mL). The resulting solution was cooled to –78 ºC with stirring and $MesBCl_2$ (1.80 g, 8.96 mmol) was added dropwise as a toluene solution (10 mL). The reaction was allowed to warm to room temperature overnight and the volatiles were removed *in vacuo*. Extraction of the residue with CH_2Cl_2 (50 mL) followed by filtration gave a yellow filtrate that was concentrated *in vacuo* to a yellow glaze. Vigorous trituration of this glaze with pentane afforded the title compound as a microcrystalline white powder that was collected on a sintered glass frit, washed with pentane and dried *in vacuo* (4.50 g, 77%). ^{1}H NMR (300 MHz, C_6D_6) δ 7.43 (d, J = 6.3 Hz, 2H), 7.26 (m, 10H), 7.00 (m, 14H), 6.91 (t, J = 7.4, 2H), 6.43 (s, 2H), 2.13 (s, 6H), 2.06 (s, 3H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$) δ 156.1 (d, J = 45.6 Hz), 143.7 (s), 142.0 (s), 140.3 (s), 139.0 (s), 138.5 (s), 135.3 (s), 134.2 (m), 133.4 (m), 129.7 (s), 128.0 (m), 127.0 (s), 24.2 (s), 21.3 (s). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ –8.5 (s). HRFABMS Calcd for $C_{45}H_{38}BP_2$ ([M–H]): 651.2542. Found: 651.2570.

[^{Mes}DPB^{Ph}]NiBr (5). $Ni(cod)_2$ (52 mg, 190 μmol) and $NiBr_2$ (42 mg, 190 μmol) were added consecutively as solids to a stirring solution of **4** (248 mg, 380 μmol) in THF (10 mL) resulting in the formation of a dark mixture which became blood red over the course of an hour. After stirring for six hours at room temperature, the volatiles were removed from the reaction *in vacuo* and the residue dissolved in benzene (3 mL). After filtration to remove a small amount of insoluble material, pentane (15 mL) was layered over the filtrate to give deep red crystals of the title compound that were separated from the mother liquor and dried *in vacuo* (201 mg, 67%). Crystals grown in this manner were suitable for X-ray diffraction. ^{1}H NMR (300 MHz, C_6D_6) δ 15.5, 11.8, 9.6, 5.5, 4.0, 1.8, –2.4, –6.11. Anal. Calcd for $C_{45}H_{39}BBrNiP_2$: C, 68.32 H, 4.97. Found: 68.42, 4.94. μ_{eff} = 1.6 B.M.

[^{Mes}DPB^{Ph}]Ni (6). Sodium (15 mg, 650 μmol) and mercury (1.5 g) were added to a scintillation vial, covered with THF (1 mL) and stirred vigorously. A solution of **5** (178 mg, 225 μmol) in THF (10 mL) was added. After 2 hours, the dark brown mixture was decanted from the mercury and the volatiles removed *in vacuo*. Extraction of the residue with benzene and filtration gave a brown solution that was lyophilized to give a brown powder. This powder was dissolved in pentane (10 mL) and allowed to stand overnight resulting in the deposition of brown crystals which were washed with pentane and dried *in vacuo* (142 mg, 89%). ^{1}H NMR (300 MHz, C_6D_6) δ 8.10 (d, J = 7.4 Hz, 2H), 7.63 (s, 4H), 7.50–7.35 (m, 2H), 7.25 (t, J = 7.4 Hz, 2H), 7.12 (s, 6H), 7.06 (t, J = 7.4 Hz, 2H),

6.84 (s, 4H), 6.78 (t, J = 7.3 Hz, 2H), 6.62 (t, J = 7.5 Hz, 4H), 5.63 (s, 2H), 1.82 (s, 3H), 1.63 (s, 6H). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$) δ 164.9, 139.5, 135.6, 134.4, 132.4, 130.9, 129.2, 128.6, 127.6, 126.1, 124.8, 25.9, 22.6. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ 25.6 (s). $^{11}B\{^1H\}$ (160 MHz, C_6D_6) δ 21.6. Anal. Calcd for $C_{45}H_{39}BNiP_2$: C, 75.99 H, 5.53. Found: 75.88, 5.79.

[^{Mes}DPB^{Ph}](H)NiH (7). A J. Young NMR tube was charged with crystals of **6** (5 mg, 7 μmol) which were then dissolved in C_6D_6 (0.7 mL). The solution was subjected to three freeze-pump-thaw cycles on a high-vacuum line and then back filled with dihydrogen (1 atm). To achieve higher pressures of dihydrogen, the entire tube was frozen with liquid nitrogen and back filled with dihydrogen (1 atm) resulting in a dihydrogen pressure of 4 atm after the sealed tube warmed to ambient temperature. ^1H NMR (300 MHz, C_6D_6) δ 7.59–7.48 (m, 10H), 7.14–6.87 (m, 18H), 6.45 (s, 2H), 2.16 (s, 3H), 2.04 (s, 6H), –6.20 (s, 1H), –15.54 (td, J = 57.8, 14.6 Hz, 1H). ^{31}P NMR (121 MHz, C_6D_6) δ 42.9 (d, $^2J_{H-P}$ = 52.1 Hz). $^{11}B\{^1H\}$ (160 MHz, C_6D_6) δ –5.0.

Catalytic hydrogenation of olefins by 6, NMR scale. In a representative experiment, **6**, ferrocene, and either styrene or *tert*-butylethylene were dissolved in C_6D_6 and transferred to a sealed J. Young NMR tube. The tube was subjected to 3 freeze-pump-thaw cycles on a high-vacuum line and back filled with dihydrogen. The reaction was then monitored by ^1H and ^{31}P NMR. In order to facilitate mixing of dihydrogen in to solution, the tube was rotated at 10–15 rpm when spectra were not being collected.

Catalytic H_2/D_2 scrambling reaction with 6. A J. Young NMR tube was charged with crystals of **6** (5 mg, 7 μmol) which were then dissolved in C_6D_6 (0.7 mL). The solution was subjected to three freeze-pump-thaw cycles on a high-vacuum line and then back filled with a 1:1 mixture of H_2 and D_2 (1 atm). HD was detected by ^1H NMR within 5 minutes. The analogous control experiment with pure solvent did not reveal any detectable scrambling.

Variable temperature van't Hoff study of the reaction of 7 with H_2. **7** and ferrocene were dissolved in toluene-d_8 and transferred to a sealed J. Young NMR tube. The tube was subjected to 3 freeze-pump-thaw cycles on a high-vacuum line and back filled with dihydrogen (1 atm). After shaking vigorously to insure mixing, the tube was inserted into a temperature controlled NMR probe and a ^1H NMR spectrum was collected at 10 K intervals from 283 K to 343 K, allowing 10 minutes for equilibration at each temperature. Concentrations of **7** and **8** were determined by integration of the mesityl aryl C–*H* resonance for the respective complexes and dihydrogen concentration was determined by direct integration of its ^1H resonance. Presuming that **7** exists as a solvent adduct in solution, the equilibrium constant of the reaction was calculated according to the expression

$$K_{obs} = \frac{[\mathbf{8}][solv]}{[\mathbf{7}][H_2]}$$

where $[C_6D_6]$ was taken to be unity. The plot of ln K_{obs} as a function of T^{-1} was fit by a line according to the expression

$$\ln K_{obs} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

The enthalpy and entropy of the reaction were extracted from the slope and intercept, respectively.

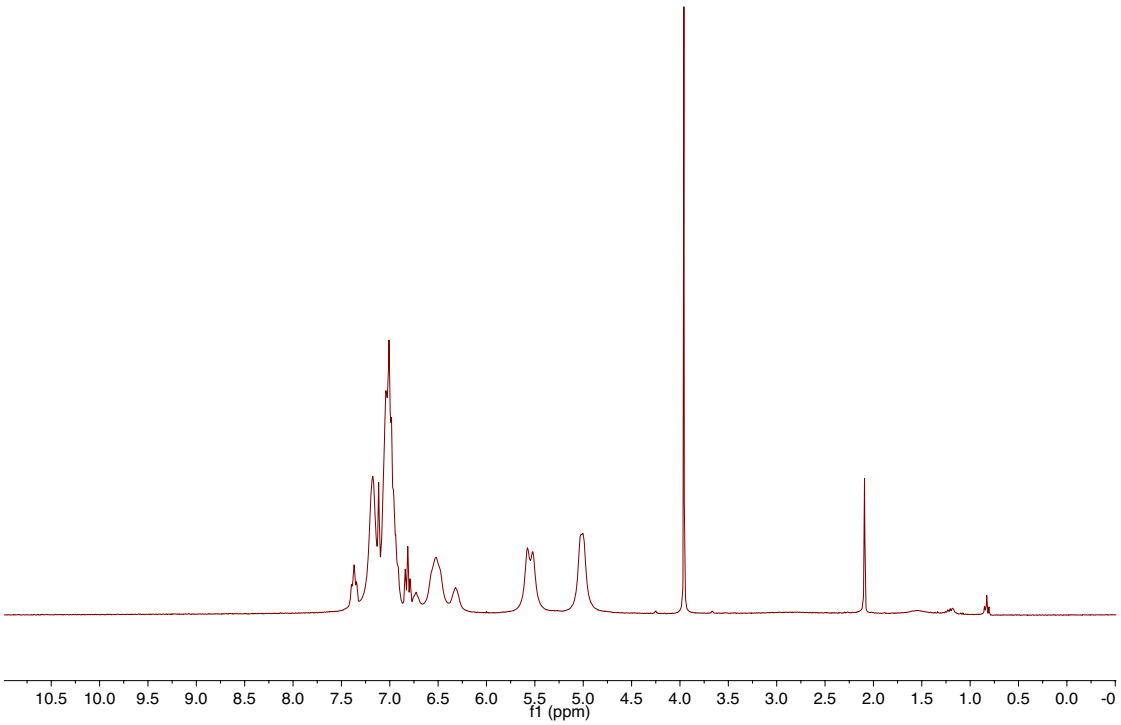

Figure S1. ^{1}H NMR spectrum of **6** in the presence of excess styrene.

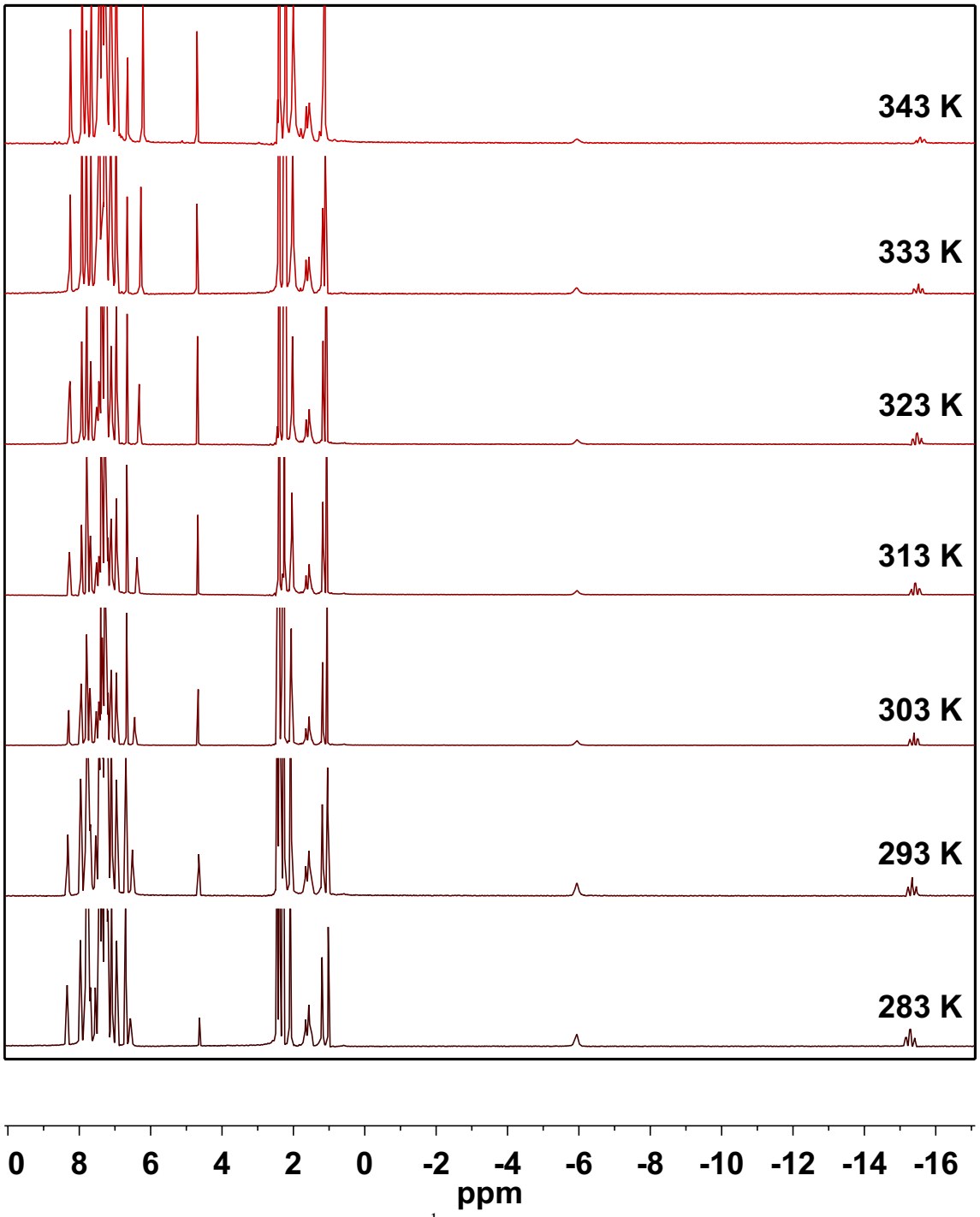

Figure S2. Variable temperature ^{1}H NMR spectra illustrating the temperature dependence of the equilibrium between **6** and **7** under H_2.

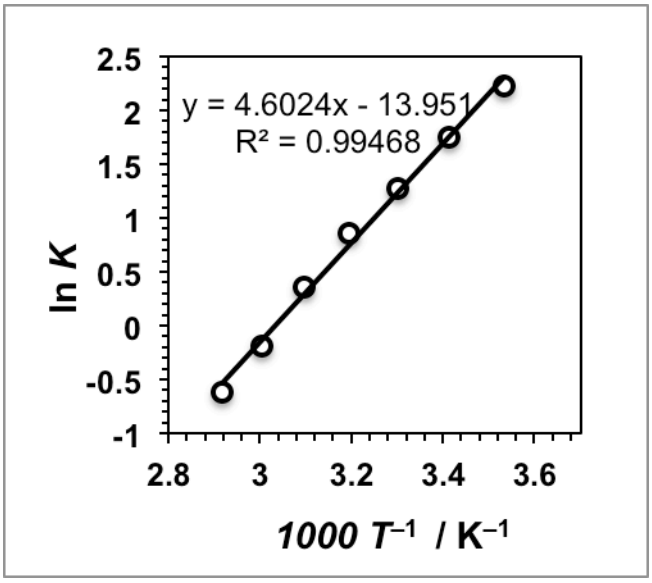

Figure S3. Van't Hoff plot derived from variable temperature ^{1}H NMR spectra of the equilibrium between **6** and **7** under 1 atm H_2 from 283–343 K.

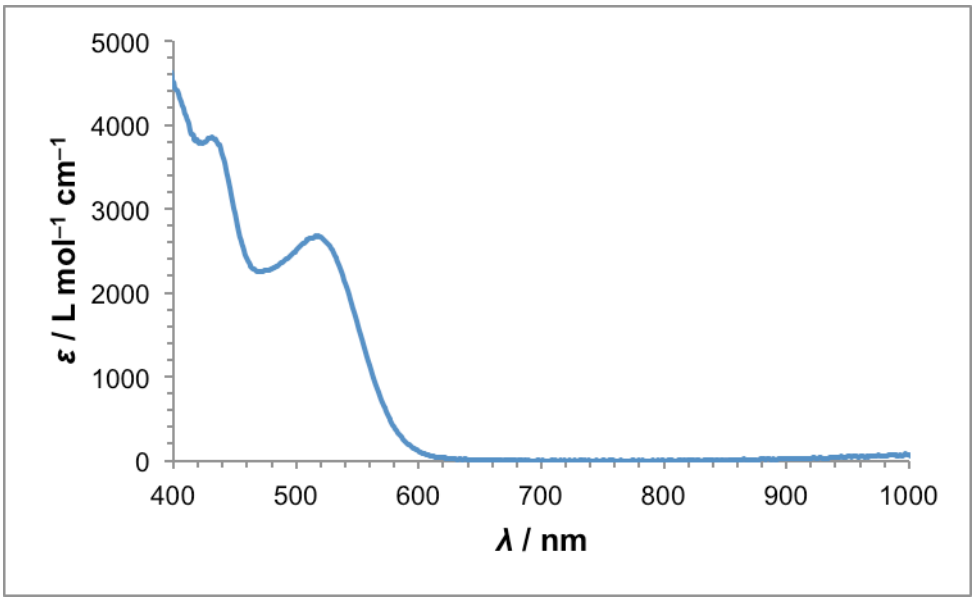

Figure S4. UV-visible spectrum of **2** in CH_2Cl_2 at room temperature.

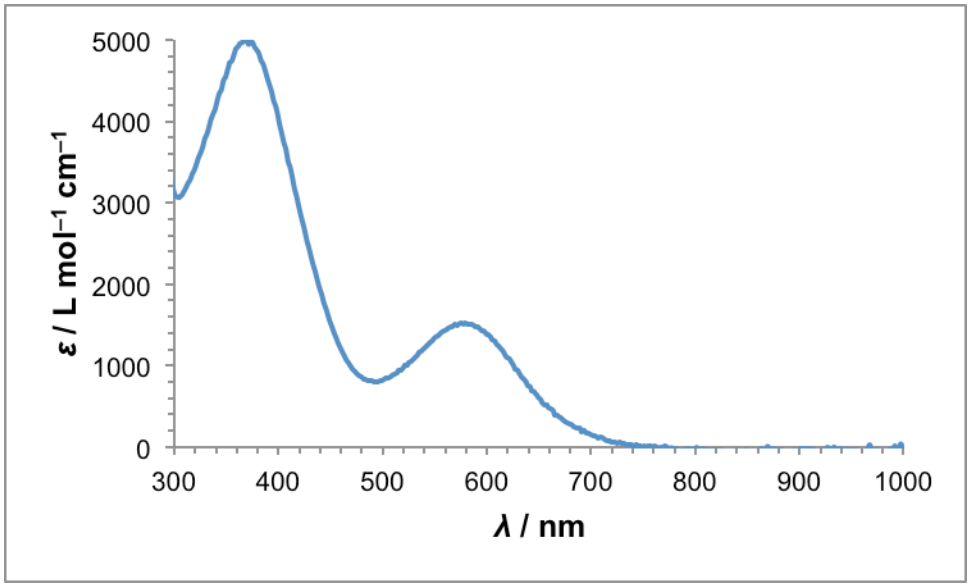

Figure S5. UV-visible spectrum of **3** in THF at room temperature.

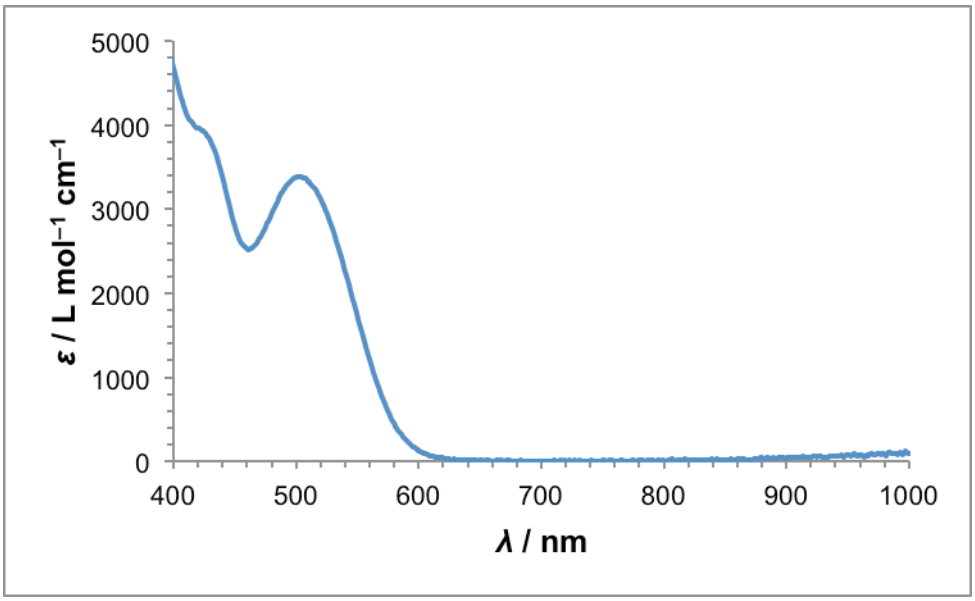

Figure S6. UV-visible spectrum of **5** in CH_2Cl_2 at room temperature.

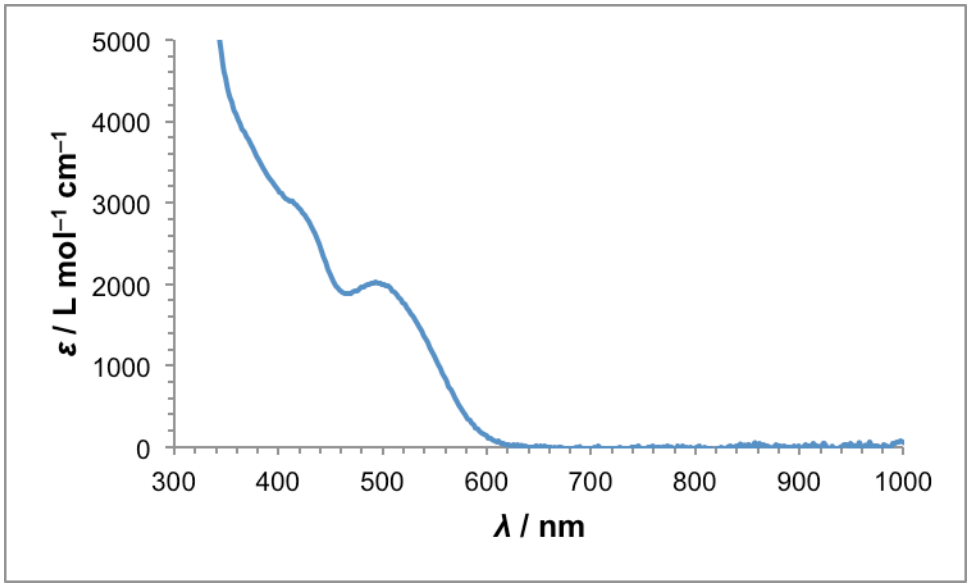

Figure S7. UV-visible spectrum of **6** in benzne at room temperature.

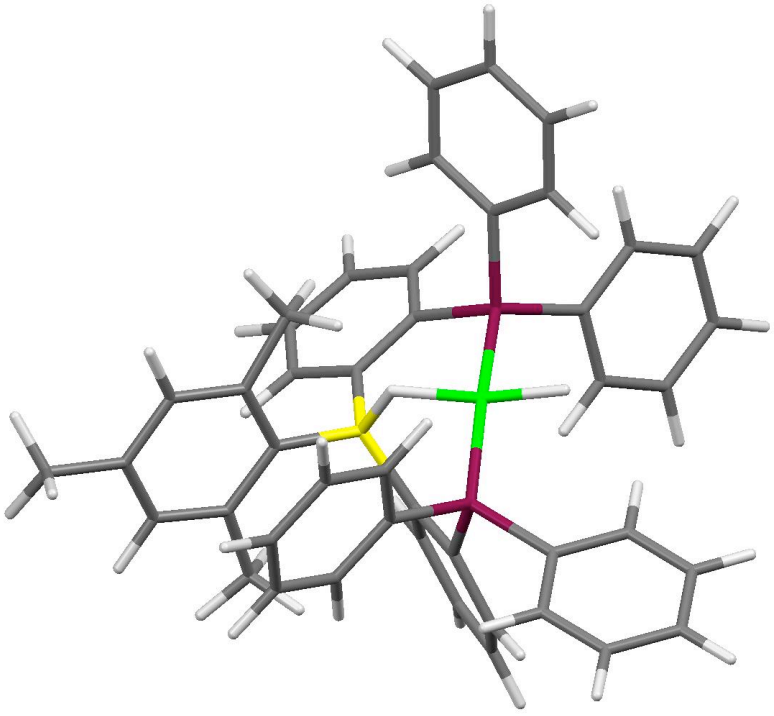

Figure S8. Lowest energy optimized structure for [^{Mes}DPB^{Ph}](H)NiH (**7**) (B3LYP/6-31G(d)).

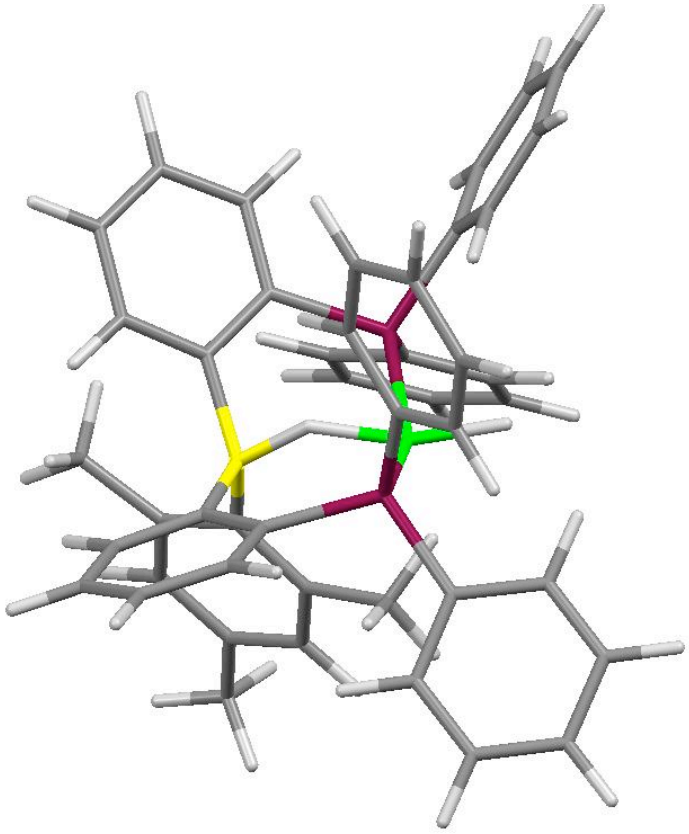

Figure S9. Higher energy isomer of [^{Mes}DPB^{Ph}](H)NiH (**7**) (BP86/6-31G(d)).

Table S1. Optimized coordinates (Å) for the more stable isomer of [^{Mes}DPB^{Ph}](H)NiH (**7**) (B3LYP/6-31G(d)).

Atom	**X**	**Y**	**Z**
Ni	-0.525780	0.648630	0.516463
H	0.163012	-0.747883	0.387072
H	-1.208603	1.867670	0.961697
P	-2.449504	-0.266132	0.309698
P	1.388118	1.646700	0.335501
C	-3.099486	-0.893418	1.909336
C	-3.332147	-2.253824	2.152957
C	-3.310897	0.031597	2.947346
C	-3.775505	-2.679162	3.407566
H	-3.166800	-2.981698	1.365706
C	-3.762243	-0.396078	4.194507
H	-3.115536	1.086796	2.775761
C	-3.994625	-1.754159	4.427910
H	-3.948939	-3.737362	3.584050
H	-3.924584	0.329862	4.986760
H	-4.339472	-2.088305	5.402798

C	-2.261142	-1.693078	-0.819911
C	-3.381281	-2.417426	-1.261677
C	-0.947516	-2.028045	-1.222667
C	-3.217496	-3.520712	-2.094669
H	-4.380371	-2.118273	-0.953091
C	-0.823340	-3.164768	-2.045151
C	-1.927861	-3.897204	-2.478972
H	-4.083268	-4.083065	-2.434662
H	0.171266	-3.483412	-2.345951
H	-1.784307	-4.764454	-3.119541
C	-3.808523	0.732230	-0.423077
C	-5.082180	0.854621	0.145506
C	-3.535747	1.385529	-1.636818
C	-6.064563	1.624084	-0.483962
H	-5.312181	0.354714	1.080995
C	-4.518362	2.149281	-2.262599
H	-2.552500	1.292440	-2.091902
C	-5.785760	2.272507	-1.686240
H	-7.048668	1.712717	-0.031073
H	-4.294283	2.650342	-3.200537
H	-6.550682	2.871280	-2.173575
C	1.223487	1.359533	-1.469299
C	0.538722	0.160365	-1.837467
C	1.485222	2.375499	-2.399935
C	0.064962	0.115465	-3.163599
C	1.053051	2.252952	-3.719365
H	2.001732	3.277848	-2.085586
C	0.314247	1.128548	-4.089846
H	-0.499018	-0.756177	-3.484661
H	1.265840	3.038978	-4.439266
H	-0.064335	1.036295	-5.105375
C	1.611207	3.459039	0.554556
C	2.885284	4.035272	0.677347
C	0.483243	4.293814	0.576168
C	3.026543	5.417428	0.811918
H	3.769168	3.405126	0.672641
C	0.628011	5.674664	0.705987
H	-0.506748	3.853909	0.501756
C	1.899334	6.239932	0.825124
H	4.019223	5.849229	0.908498
H	-0.254728	6.308346	0.722416
H	2.010354	7.315661	0.933358
C	2.936740	0.919457	0.982657
C	4.003051	0.552154	0.152505
C	3.055249	0.750926	2.371121
C	5.171356	0.023937	0.703953

H	3.913623	0.665348	-0.923427
C	4.225468	0.228965	2.919569
H	2.227641	1.025340	3.021224
C	5.285107	-0.135470	2.085559
H	5.988293	-0.270722	0.051326
H	4.307610	0.099796	3.995433
H	6.194772	-0.549816	2.512048
B	0.363443	-1.131387	-0.834799
C	1.695676	-2.063321	-0.573000
C	1.823723	-2.743528	0.672809
C	2.707865	-2.320411	-1.536736
C	2.915842	-3.577872	0.934826
C	3.786177	-3.167390	-1.237401
C	3.923035	-3.798593	-0.003800
H	2.974872	-4.076644	1.901545
H	4.540200	-3.342264	-2.004000
C	0.795076	-2.618555	1.780621
H	0.817920	-1.630033	2.258224
H	-0.226420	-2.771895	1.417949
H	0.983721	-3.361585	2.563001
C	2.702692	-1.736635	-2.938103
H	1.772217	-1.946513	-3.474277
H	2.824396	-0.648382	-2.943515
H	3.522428	-2.162398	-3.527127
C	5.110603	-4.678842	0.308409
H	5.862521	-4.143355	0.904688
H	4.816305	-5.563185	0.885928
H	5.605956	-5.023349	-0.606051

Total Energy [a.u.]: -3955.2402934

Table S2. Optimized coordinates (Å) for the most lower energy isomer of [^{Mes}DPB^{Ph}](H)NiH (**7**) (BP86/6-31G(d)).

Atom	**X**	**Y**	**Z**
Ni	-0.505176	0.613646	0.300089
H	0.105980	-0.801477	0.560924
H	-1.221353	1.872968	0.600024
P	-2.429628	-0.273853	0.306165
P	1.394260	1.631099	0.269526
C	-2.994922	-0.683030	2.013322
C	-3.088449	-2.011578	2.475335
C	-3.278210	0.378614	2.902984
C	-3.462846	-2.272275	3.804160

H	-2.871333	-2.841197	1.794476
C	-3.659933	0.112657	4.224651
H	-3.193794	1.415047	2.555298
C	-3.750952	-1.214658	4.679505
H	-3.529649	-3.309168	4.153145
H	-3.879936	0.943865	4.904439
H	-4.042257	-1.421456	5.715595
C	-2.267522	-1.861459	-0.606113
C	-3.383410	-2.662584	-0.926315
C	-0.941933	-2.226902	-0.969103
C	-3.195465	-3.879896	-1.596666
H	-4.394920	-2.338784	-0.651111
C	-0.792710	-3.471385	-1.624279
C	-1.893608	-4.284479	-1.937939
H	-4.057750	-4.509627	-1.845059
H	0.217673	-3.806615	-1.888875
H	-1.736745	-5.239463	-2.454357
C	-3.862749	0.600422	-0.458407
C	-5.174775	0.499361	0.048756
C	-3.631778	1.353075	-1.630207
C	-6.237877	1.144867	-0.604048
H	-5.365431	-0.073567	0.962891
C	-4.696923	1.992602	-2.280097
H	-2.614517	1.434796	-2.031599
C	-6.001653	1.891574	-1.768312
H	-7.252795	1.063477	-0.197836
H	-4.505881	2.576425	-3.187873
H	-6.831773	2.397071	-2.274972
C	1.064172	1.273713	-1.503707
C	0.315600	0.054737	-1.729447
C	1.179528	2.271639	-2.496120
C	-0.348208	-0.023151	-2.987253
C	0.571216	2.101169	-3.746393
H	1.735105	3.190887	-2.278184
C	-0.217095	0.958869	-3.977213
H	-0.960301	-0.908690	-3.195529

H	0.690927	2.863005	-4.525481
H	-0.727587	0.831614	-4.939935
C	1.594605	3.458433	0.415680
C	2.874305	4.055857	0.397652
C	0.454774	4.281327	0.533080
C	3.005990	5.450678	0.483268
H	3.769055	3.428725	0.319879
C	0.590701	5.674607	0.614452
H	-0.538442	3.817490	0.562483
C	1.866104	6.262786	0.590987
H	4.004739	5.902046	0.467661
H	-0.303291	6.302115	0.706179
H	1.971310	7.351396	0.662732
C	3.002371	0.961642	0.844130
C	4.005657	0.549566	-0.054705
C	3.243429	0.906171	2.233868
C	5.238096	0.088749	0.433372
H	3.813179	0.576650	-1.132373
C	4.478519	0.450744	2.716234
H	2.460809	1.218721	2.936252
C	5.476959	0.042510	1.816078
H	6.009569	-0.242556	-0.270341
H	4.659603	0.408361	3.796379
H	6.440267	-0.318716	2.193880
B	0.317781	-1.222624	-0.694844
C	1.735326	-2.012373	-0.481473
C	2.048587	-2.589312	0.791391
C	2.640217	-2.295862	-1.549718
C	3.216834	-3.350665	0.977617
C	3.800222	-3.068444	-1.326843
C	4.119539	-3.598432	-0.069124
H	3.421174	-3.772604	1.971883
H	4.470695	-3.269438	-2.174668
C	1.139378	-2.423433	1.997545
H	1.126366	-1.381123	2.370402
H	0.091586	-2.689816	1.768073

H	1.474797	-3.068280	2.829416
C	2.414571	-1.816438	-2.975610
H	1.416168	-2.093760	-3.356524
H	2.485873	-0.717825	-3.071443
H	3.165314	-2.260121	-3.654031
C	5.377423	-4.414070	0.152694
H	6.109970	-3.870726	0.780740
H	5.159933	-5.366951	0.670462
H	5.875604	-4.656003	-0.802678

Total Energy [a.u.]: -3955.4856232

Table S3. Optimized coordinates (Å) for higher energy isomer of [^{Mes}DPB^{Ph}](H)NiH (**7**) (BP86/6-31G(d)).

Atom	**X**	**Y**	**Z**
Ni	0.346500	0.274204	-0.801421
H	0.207040	-0.096231	0.623311
H	0.763239	1.103345	-1.969012
P	2.339408	-0.290550	-0.276261
P	-1.420586	1.391787	-0.344231
C	3.327317	-1.142290	-1.583162
C	3.765351	-2.479190	-1.485065
C	3.557766	-0.432997	-2.785607
C	4.437896	-3.085647	-2.559447
H	3.577549	-3.050698	-0.570477
C	4.242233	-1.037698	-3.848737
H	3.179889	0.591020	-2.890052
C	4.685089	-2.367173	-3.738365
H	4.767738	-4.127185	-2.470340
H	4.418220	-0.473531	-4.771879
H	5.210468	-2.843188	-4.574060
C	2.267256	-1.425462	1.192364
C	3.468463	-1.937239	1.733836
C	0.997324	-1.764871	1.745781
C	3.436748	-2.838056	2.805997

H	4.433960	-1.626948	1.315103
C	1.008509	-2.707078	2.804198
C	2.195686	-3.236989	3.329169
H	4.371094	-3.232228	3.221979
H	0.052440	-3.039936	3.225966
H	2.154177	-3.958160	4.154482
C	3.402162	1.104021	0.312828
C	4.666329	1.418684	-0.222578
C	2.890753	1.883794	1.375745
C	5.401373	2.502191	0.287907
H	5.081930	0.817866	-1.038406
C	3.629495	2.960798	1.883809
H	1.912776	1.641205	1.810276
C	4.886269	3.275745	1.338424
H	6.383786	2.736848	-0.138307
H	3.221903	3.556096	2.708910
H	5.462137	4.119964	1.734475
C	-1.637195	1.249363	1.506253
C	-1.032695	0.134832	2.163419
C	-2.248058	2.288379	2.236894
C	-0.978769	0.187020	3.572961
C	-2.220220	2.277451	3.640399
H	-2.705622	3.135095	1.712222
C	-1.556690	1.236492	4.306536
H	-0.466479	-0.619126	4.113048
H	-2.680286	3.097443	4.203897
H	-1.484522	1.241985	5.401074
C	-1.351844	3.213759	-0.657712
C	-2.509391	3.987030	-0.890233
C	-0.094894	3.853530	-0.624302
C	-2.409343	5.374716	-1.080927
H	-3.490514	3.501225	-0.934487
C	0.000961	5.240600	-0.808554
H	0.810123	3.254561	-0.467096
C	-1.155414	6.004296	-1.038002
H	-3.315372	5.963417	-1.266329

H	0.984276	5.724182	-0.782489
H	-1.078659	7.087132	-1.189877
C	-3.011674	0.889177	-1.129556
C	-4.071472	0.323447	-0.394676
C	-3.139807	1.035767	-2.529540
C	-5.245567	-0.082466	-1.049527
H	-3.974145	0.196600	0.688374
C	-4.315602	0.634516	-3.177905
H	-2.313814	1.468084	-3.107466
C	-5.371561	0.073923	-2.438212
H	-6.062703	-0.525928	-0.469297
H	-4.406774	0.754983	-4.263642
H	-6.288860	-0.244922	-2.946423
B	-0.389329	-1.070622	1.236437
C	-1.474768	-2.107835	0.573387
C	-2.553723	-2.652383	1.342400
C	-1.358529	-2.604031	-0.763434
C	-3.445065	-3.592215	0.780818
C	-2.267839	-3.536713	-1.292525
C	-3.336004	-4.045512	-0.539050
H	-4.257861	-3.982103	1.409512
H	-2.133467	-3.876482	-2.328910
C	-2.834776	-2.287897	2.792706
H	-1.940353	-2.350733	3.434661
H	-3.219715	-1.258419	2.902975
H	-3.590622	-2.972372	3.217094
C	-0.238105	-2.177218	-1.687080
H	-0.268282	-1.077365	-1.929853
H	0.757143	-2.435700	-1.285726
H	-0.321930	-2.669130	-2.672694
C	-4.326176	-5.027436	-1.130039
H	-3.824045	-5.776790	-1.768879
H	-4.878662	-5.568582	-0.341758
H	-5.075705	-4.515242	-1.764467

Total Energy [a.u.]: -3955.4604723

Table S4. Crystal data and structure refinement for **2**.

Compound	[^{Ph}DPB^{Ph}]NiBr	
Empirical formula	$C_{42}H_{33}BBrNiP_2$	
Formula weight	749.05	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P–1	
Unit cell dimensions	a = 9.5770(5) Å	α = 87.226(3)º
	b = 9.8305(5) Å	β = 89.257(3)º
	c = 19.7127(10) Å	γ = 68.802(3)º
Volume	1728.26(15) Å^3	
Z	2	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	1.840 mm^{-1}	
F(000)	766	
Crystal size	0.34 x 0.23 x 0.09 mm^3	
Theta range for data collection	2.07 to 39.28°	
Index ranges	$-16 \le h \le 16$, $-17 \le k \le 17$, $-34 \le l \le 34$	
Reflections collected	150487	
Independent reflections	19771 [R_{int} = 0.0380]	
Completeness to θ = 39.28º	96.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8519 and 0.5735	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19771 / 0 / 424	
Goodness-of-fit on F^2	1.124	
Final R indices [$I > 2\sigma_I$]	R_1 = 0.0380, wR_2 = 0.0945	
R indices (all data)	R_1 = 0.0517, wR_2 = 0.0990	
Largest diff. peak and hole	2.259 and –0.850 e.Å^{-3}	

Table S5. Crystal data and structure refinement for **3**.

Compound	[^{Ph}DPB^{Ph}]Ni(THF)	
Empirical formula	$C_{46}H_{41}BNiOP_2$	
Formula weight	741.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	*Cc*	
Unit cell dimensions	a = 23.7152(11) Å	α = 90º
	b = 11.0648(5) Å	β = 129.973(2)º
	c = 18.3257(8) Å	γ = 90º
Volume	3685.3(2) Å^3	
Z	4	
Density (calculated)	1.340 Mg/m^3	
Absorption coefficient	0.652 mm^{-1}	
F(000)	1552	
Crystal size	0.23 x 0.22 x 0.10 mm^3	
θ range for data collection	2.16 to 32.61°.	
Index ranges	$-35 \le h \le 35$, $-13 \le k \le 16$, $-27 \le l \le 27$	
Reflections collected	45429	
Independent reflections	13192 [R(int) = 0.0533]	
Completeness to θ = 32.57º	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9377 and 0.8646	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13192 / 2 / 460	
Goodness-of-fit on F^2	1.034	
Final *R* indices [$I > 2\sigma_I$]	R_1 = 0.0408, wR_2 = 0.0895	
R indices (all data)	R_1 = 0.0548, wR_2 = 0.0958	
Absolute structure parameter	–0.001(7)	
Largest diff. peak and hole	1.186 and –0.764 e.Å^{-3}	

Table S6. Crystal data and structure refinement for **5**.

Compound	[^{Mes}DPB^{Ph}]NiBr
Empirical formula	$C_{45}H_{39}BBrNiP_2$
Formula weight	791.13
Temperature	100(2) K

Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.4313(10) Å	$\alpha = 90^o$
	b = 14.5190(10) Å	$\beta = 102.722(2)^o$
	c = 20.8242(14) Å	$\gamma = 90^o$
Volume	3666.3(5) $Å^3$	
Z	4	
Density (calculated)	1.433 Mg/m^3	
Absorption coefficient	1.739 mm^{-1}	
F(000)	1628	
Crystal size	0.35 x 0.29 x 0.28 mm^3	
θ range for data collection	2.19 to 39.12°.	
Index ranges	$-21 \le h \le 18, -25 \le k \le 25, -36 \le l \le 36$	
Reflections collected	122877	
Independent reflections	20779 [$R_{int} = 0.0458$]	
Completeness to $\theta = 39.12^o$	96.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6417 and 0.5812	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20779 / 0 / 454	
Goodness-of-fit on F^2	1.015	
Final R indices [$I > 2\sigma_I$]	$R_1 = 0.0350$, $wR_2 = 0.0809$	
R indices (all data)	$R_1 = 0.0616$, $wR_2 = 0.0900$	
Largest diff. peak and hole	0.742 and -0.657 e.$Å^{-3}$	

Table S7. Crystal data and structure refinement for **6**.

Compound	[^{Mes}DPB^{Ph}]Ni	
Empirical formula	$C_4 H_{39}BNiP_2$	
Formula weight	711.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P-1$	
Unit cell dimensions	a = 9.9796(5) Å	$\alpha = 73.940(3)°$.
	b = 13.1425(7) Å	$\beta = 87.331(3)°$.

	c = 14.6968(7) Å $\gamma = 69.709(3)°$.
Volume	1734.80(15) $Å^3$
Z	2
Density (calculated)	1.362 Mg/m^3
Absorption coefficient	0.685 mm^{-1}
F_{000}	744
Crystal size	0.25 x 0.19 x 0.12 mm^3
θ range for data collection	1.91 to 39.28°
Index ranges	$-17 \le h \le 17, -23 \le k \le 23, -25 \le l \le 25$
Reflections collected	107430
Independent reflections	19730 [$R_{int} = 0.0360$]
Completeness to $\theta = 39.28°$	96.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9224 and 0.8475
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19730 / 0 / 445
Goodness-of-fit on F^2	0.982
Final R indices [$I > 2\sigma_I$]	$R_1 = 0.0304$, $wR_2 = 0.0829$
R indices (all data)	$R_1 = 0.0454$, $wR_2 = 0.0867$
Largest diff. peak and hole	0.818 and -0.242 $e.Å^{-3}$